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A life cycle assessment of options for producing synthetic fuel via pyrolysis

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Abstract

The aim of this study was to investigate the sustainability of producing synthetic fuels from biomass using thermochemical processing and different upgrading pathways. Life cycle assessment (LCA) models consisting of biomass collection, transportation, pre-treatment, pyrolysis and upgrading stages were developed. To reveal the environmental impacts associated with greater post-processing to achieve higher quality fuels, six different bio-oil upgrading scenarios were analysed and included esterification, ketonisation, hydrotreating and hydrocracking. Furthermore, to take into account the possible ranges in LCA inventory data, expected, optimistic and pessimistic values for producing and upgrading pyrolysis oils were evaluated. We found that the expected carbon dioxide equivalent emissions could be as high 6000 gCO_{2e}/kg of upgraded fuel, which is greater than the emissions arising from the use of diesel fuel. Other environmental impacts occurring from the fuel production process are outlined, such as resource depletion, acidification and eutrophication.

Keywords: Biofuel; environmental impact; thermochemical conversion; bio-oil upgrading; global warming potential (GWP); life cycle assessment (LCA).

1. Introduction

Approximately 5% of the global transportation demand is met by biofuels, and biomass is set to play an increasingly important role in reducing transport related CO_2 emissions. Currently, the majority of biofuels used for transportation are derived from food crops; this has raised fears of increasing food prices and causing food shortages. There are also concerns with the environmental impacts of using large quantities of fertilizers and pesticides to cultivate certain energy crops (IEA, 2011).

Biofuels can be obtained from fast-growing non-food crops, agricultural residues and other waste feedstock. These fuels are often referred to as second-generation biofuels, and they are generally considered more sustainable and environmentally friendly. However, producing second-generation biofuels involves more complex and energy intensive conversion processes. Whilst a significant amount of research has been carried out on the use of first-generation biofuels for transportation, research on second-generation fuels is more limited.

There is a range of biochemical and thermochemical processes for converting waste biomass into second-generation biofuels. The thermochemical conversion methods include pyrolysis, liquefaction and gasification, and products from these processes require significant amounts of upgrading to improve their quality. Pyrolysis involves the thermal degradation of matter in the absence of oxygen to produce bio-oil, non-condensable gases and a solid char residue. It has gathered much interest as a promising option for producing synthetic transportation fuels. However, bio-oil from pyrolysis is highly oxygenated, unstable and acidic. This means that the bio-oil quality has to be improved before it can be used as a transportation fuel (Ringer,

Putsche and Scahill, 2006). There are a number of upgrading methods, which are being investigated to improve pyrolysis oils. Yet, even if a perfect transportation fuel from pyrolysis can be obtained, it has to offer environmental benefits in comparison to conventional fossil fuels.

The environmental impacts of obtaining transportation fuels from a pyrolysis process can be analysed by conducting life cycle assessment (LCA). LCA enables comparisons to be made with fossil fuels and other technological options for producing biofuels. A number of LCA studies on fuels obtained from pyrolysis and other thermochemical conversion processes have been carried out. Iribarren et al. (2012) conducted a life cycle assessment of pyrolysis coupled with hydrotreating. They concluded that the highest impacts were associated with the use of electricity for feedstock processing and natural gas for obtaining hydrogen through steam reforming. Snowden-Swan and Male (2012) conducted a study on pyrolysis with hydrotreating of poplar residues and found the carbon dioxide equivalent (CO_{2e}) emissions to be 32.5 gCO_{2e}/MJ. Peters et al. (2015) simulated a pyrolysis plant and biorefinery for fast pyrolysis of hybrid poplar. An LCA analysis was conducted to see if hydrotreating, hydrocracking, distillation or steam reforming had a more negative impact on the environment. They found that the key contributors to greenhouse gas (GHG) emissions were the pyrolysis plant and the biorefinery, suggesting that the environmental impact could be improved by seeking ways to reduce the electricity consumption. Dang et al. (2014) and Zang et al. (2014) investigated alternative sources of hydrogen for upgrading pyrolysis oils. For conventional natural gas reforming, their results indicated that the GHG emissions would be in the region of 30–40 gCO_{2e}/MJ. In comparison, GHG emissions associated with the use of conventional transportation fuels is around 94 CO_{2e}/MJ.

The majority of LCA studies on biofuels obtained from pyrolysis have focused on considering pyrolysis with hydroprocessing (Peters, Iribarren and Dufour, 2015; Dang, Yu

and Luo, 2014; Zhang, 2014; Iribarren, Peters and Dufour, 2012; Snowden-Swan and Male, 2012). However, the structural complexity of bio-oil makes it difficult to find a single comprehensive upgrading method; therefore, there is a rising interest in using a synergy of technologies. There are many upgrading options and additional processing stages, which must be considered if fuels of a comparable quality to fossil fuels are to be obtained. It is also difficult to compare LCA studies that have considered different upgrading methods. The assumptions made among studies vary, such as the feedstock type, pyrolysis technology and processing conditions (e.g. slow, intermediate and fast pyrolysis). LCA results are also highly subjective and variable, and there is often a lack of transparency with the data used.

This study aims to analyse the environmental impacts of the main emerging bio-oil upgrading technologies, so that a more informed comparison can be made to guide future R&D on obtaining synthetic fuel from pyrolysis. Moreover, the possible range in LCA data needs to be investigated to highlight the sensitivity of the results. This will enable a combination of pyrolysis and upgrading methods to be identified, which give good fuel yields and quality, whilst still offering environmental benefits in comparison to fossil fuels.

In the following section, the method adopted for this study is outlined and the pyrolysis upgrading scenarios are defined. Gathered LCA inventory data, including possible ranges in values, are presented in Section 2.2. The LCA results are outlined and discussed in Section 3.

2. Materials and methods

Different bio-oil upgrading methods are initially reviewed to identify the most promising combination of processes to pursue. An outcome from this is six scenarios to be analysed and compared in terms of their environmental impact.

A life cycle assessment of each scenario is performed using GaBi Professional with the integrated Ecoinvent database. A well-to-wheel analysis is adopted to consider all the resource inputs and outputs from biomass cultivation to fuel combustion in a vehicle. The LCA system boundary also includes biomass transportation, biomass preparation, an integrated bio-oil production and upgrading plant, and fuel transportation (see Figure 1). The functional unit used to compare the alternative scenarios is one kilogram of upgraded fuel. One mega joule of energy content of the upgraded fuel is not used due to the uncertainties of fuel quality in certain scenarios, but conversions are made where data is available.

To enable the alternative upgrading scenarios to be compared, a fixed feedstock and pyrolysis processing technology is used throughout. Corn stover is analysed as it has been considered as a suitable waste feedstock for pyrolysis in a range of studies (Dang, Yu and Luo, 2014; Zhang, 2014). The fluidised bed reactor operating under fast pyrolysis conditions is assumed as it is a popular option due to its ease of operation, high stability under pyrolysis conditions and high oil yields (Ringer, Putsche and Scahill, 2006).

Assessing the environmental impacts of obtaining fuel from residual stover waste is challenging as different allocation methods can have a significant impact on the LCA results. Previous researches on corn stover have had a tendency to use subdivision to avoid allocation to corn grain and subsequent co-products (Murphy and Kendall, 2013). This study assumes changes to an existing continuous corn production system and assigns additional processes for the collection and nutrient replacement of partially gathered stover, which would have

otherwise been left unharvested. Subdivision of the co-products arising in each scenario is difficult due to the lack of data and established practices with using pyrolysis products and synthetic fuels. Methods adopted in previous studies include no allocation to the by-products—due to the large uncertainties—and mass-, energy- and value- based approaches (Kendall and Chang, 2009; Larson, 2006). In this study, the total energy and material inputs consumed in the production of by-products are included. Where possible, the by-products are used within the system (e.g. heat generation from the pyrolysis gases). Displacement of energy had the production of the by-products been made via other routes and their market worth are not considered.

Due to model uncertainties, where possible, minimum, expected and maximum values have been obtained for each stage of the LCA analysis from the literature, GaBi Professional databases and Ecoinvent 3.3. This allows the most likely values and possible ranges to be obtained in terms of the environmental impacts of each upgrading stage. The sensitivity of the results based on fertiliser and hydrogen usage are further examined. The global warming potential (GWP) of each processing stage and utilised resource is investigated and other environmental impact categories are evaluated based on the CML2001 impact assessment method (Guinée, 2002).

2.1 Definition of the bio-oil upgrading scenarios

To upgrade bio-oil obtained through the pyrolysis of biomass, there are a number of physical (filtration, solvent addition and emulsification) and catalytic and chemical methods (hydrotreating, hydrocracking, esterification, ketonisation, and gasification to syngas followed by Fischer-Tropsch). This study focuses on the pyrolysis process and catalytic and

chemical upgrading methods. Gasification with Fischer-Tropsch is considered to be beyond the scope of the study.

The process of hydrotreating and hydrocracking is often referred to as hydroprocessing. Hydrotreating involves the use of hydrogen and catalysts to reduce levels of sulphur, nitrogen and oxygen. The process takes place at relatively modest temperatures (150^{o}C–400^{o}C) (Gandarias and Arias, 2013) and is also known as hydrodeoxygenation. Depending on the amount of hydrotreating performed, different degrees of deoxygenation can be achieved. Two-stage hydrotreating can also be carried out which has the potential to achieve higher degrees of deoxygenation, reduce hydrogen consumption and overcome bio-oil instability issues. The first stage, takes place at a relatively low temperature (270ºC) and hydrotreating is performed at a higher temperature (350ºC) in the second stage (Elliott, 2007). Once bio-oil has been hydrotreated, it can be hydrocracked to break carbon-carbon bonds and converted into shorter-chain hydrocarbons, which are more suitable as transportation fuels.

A promising option for improving bio-oil quality prior to hydrotreating is esterification (Ciddor et al., 2015). Bio-oil produced from biomass normally has a high oxygen content (20–50wt %) and acidity (pH=2.5–3), resulting in a low heating value (16–18MJ/kg), high viscosity and corrosiveness. Esterification reduces acidity by neutralising carboxylic acids in the bio-oil; this improves stability and reduces catalyst deactivation and hydrogen consumption during hydrotreating. Another pre-hydrotreating method is ketonisation, which is a condensation reaction that enables the partial reduction of oxygen in the form of water (Milina, Mitchell and Pérez-Ramírez, 2014). Ketonisation is a reaction that transforms two carboxylic acids into a ketone, carbon dioxide and water (Pham et al., 2013). Ketonisation also removes highly reactive shorter carboxylic acids, by converting acetic acid into acetone, and increases the size of carbon chains, which improves product stability. Furthermore, acetone can be converted, along with other bio-oil components, into longer chain

hydrocarbons through aldol condensation and subsequent hydrogenation; this prevents small molecules being lost in the form of light gases (Pham et al., 2013; Pham et al., 2012). Ketonisation can be performed on pyrolysis vapours, but conducting ketonisation on the liquid phase minimises decomposition and re-polymerisation of the bio-oil. Phase separation is required to obtain light oxygenates for the ketonisation process, and this can be followed by aldol condensation (Pham et al., 2012). The sugar and lignin derived components can then undergo esterification.

Based on the reviewed upgrading methods, six alternative scenarios are developed: i) hydrotreating and hydrocracking; ii) esterification, hydrotreating and hydrocracking; iii) esterification/ketonisation, hydrotreating and hydrocracking; iv) two-stage hydrotreating and hydrocracking; v) esterification, two-stage hydrotreating and hydrocracking, and vi) esterification/ketonisation, two-stage hydrotreating and hydrocracking. Scenarios 1 and 4 have been outlined in numerous studies and several LCA studies of scenario 1 have been performed by other researchers (Peters, Iribarren and Dufour, 2015; Dang, Yu and Luo, 2014; Zhang, 2014; Iribarren, Peters and Dufour, 2012; Snowden-Swan and Male, 2012). A few authors have considered introducing esterification into the upgrading process (scenarios 2 and 5), but the environmental impacts were not evaluated (Ciddor et al., 2015; Milina, Mitchell and Pérez-Ramírez, 2014). More recently, ketonisation and aldol condensation have been suggested (Milina, Mitchell and Pérez-Ramírez, 2014), and scenarios 3 and 6 are extensions of a process proposed by Pham et al. (2014). The bio-oil production process and the six upgrading scenarios to be analysed are outlined in Figure 2, and their main differences are summarised in Table 1.

2.2 Inventory data

The inventory data gathered and used for modelling each stage of the system is now outlined.

2.2.1 Feedstock cultivation, collection and transport

The inventory data associated with corn cultivation depends on the assumed soil conditions and anticipated crop yields. The majority of corn fields are treated with fertiliser to meet the high demand of nitrogen, phosphate and potassium in corn cultivation, and additional requirements are needed when corn stover is removed. Crop rotation is not considered, which could reduce these requirements. Most LCA studies on corn stover use an allocation approach based on nutrient replacement, with stover comprising 0.8% N, 0.2% P_2O_5, and 1.45% K_2O. For a crop yield of 147 bushels/acre, 1.6 dry tonnes/acre of stover can be sustainably gathered, as a stover collection rate of 40% is considered suitable to avoid soil quality degradation (Murphy and Kendall, 2013). Annual fertiliser application rates are determined based on common fertiliser nutrient composition: ammonium phosphate nitrate (8% N, 52% P_2O_5), ammonium nitrate (35% N) and potassium chloride (60% K_2O). Field emissions arising from the denitrification process by soil micro-organisms are taken as 1.25% g N_2O/ g N: all the emissions allocated to K, N and P are provided in Nemecek et al. (2007).

Direct land use change emissions depend on soil characteristic baseline assumptions. Carbon stored in soil can be released during field preparations or sequestered in degraded soils; however, stover removal is expected to reduce potential carbon sequestration. Most studies do not include land change emissions, assuming existing corn cropland would be used for gathering stover (Larson, 2006); however, land emissions could have a significant impact and should be considered in specific site evaluations.

The energy requirement for cutting, baling, field transport and on-site storage of the stover has been reported to range from 0.22 (Dang, Yu and Luo, 2014) to 0.83 MJ/kg of stover (Murphy and Kendall, 2013). This study assumes that this demand would be met with diesel fuel. The grain is not considered within the system boundary and therefore the additional fertiliser and energy requirements for gathering corn grain are not included.

Subsequent transportation would be required to take the raw feedstock from a collection point to the bio-oil production plant. The transportation distance is assumed to range from 50–100 km, with 75 km being the most likely value. A 9.3 t payload truck from the GaBi Professional database has been used to meet this transportation requirement, which is equivalent to minimum, expected and maximum diesel usages of 0.05, 0.075 and 0.1 MJ/kg of delivered corn stover, respectively (GaBi, 2017).

2.2.2 Pre-treatment

Pre-treatment of the feedstock prior to pyrolysis involves grinding and drying to reduce particle size and moisture content. Mechanical feedstock size reduction is required because fluidized bed reactors are designed to use small particles ranging from 2-3 mm. The expected energy for grinding and chopping is expected to range from 0.011–0.057 kWh/kg (Mani, Tabil and Sokhansanj, 2004; Zhang, 2014). To improve reactor temperature stability and reduce pyrolysis processing energy requirements, the moisture content needs to be reduced to less than 10% (Bridgwater and Peacocke, 2000), and this can be achieved using steam and a trommel. Zhang (2014) assumes a steam requirement of 0.085 kg/kg of pre-treated corn stover and Dang et al. (2014) state an energy requirement of 0.148 kWh/kg of pre-treated corn stover. The pyrolysis non-condensable gases (NCG) are expected to have an HHV of 6 MJ/kg and yields of 10-20% are typical (Mullen et al., 2010); thus there would be sufficient gas to combust to meet this demand. For higher pyrolysis oil yields, both the gas and char may need to be used. Using the pyrolysis gases for drying has been assumed in other studies (Peters, Iribarren and Dufour, 2015; Han et al., 2011), and therefore the energy requirement is often neglected.

2.2.3 Pyrolysis process

The pyrolysis plant is assumed to process 2000 metric tons per day of prepared corn stover at 500 °C (Wright et al., 2010; Zhang, 2014). Electricity is typically used as the energy input to a pyrolysis system, with power requirements ranging from 0.14–0.487 kWh/kg of bio-oil produced (Dang, Yu and Luo, 2014; Zhang, 2014). A value of 0.417 is suggested in (Zhang, 2014), which has been chosen as the expected value. The yield of bio-oil from the fast pyrolysis of corn stover is typically around 62-75 wt% (Dang, Yu and Luo, 2014; Zhang, 2014; Han et al., 2011), although yields as high as 80% have been suggested (Bulushev and Ross, 2011).

2.2.4 Esterification

Esterification is performed within a temperature range of 70–170^{o}C (Gunawan et al., 2012). The yield of upgraded bio-oil in conventional conditions (100 ^{o}C) when using a zeolite catalyst is approx. 62 wt% (Peng et al., 2009). Ideal ethanol to oil ratios of 3:1 (Bulushev and Ross, 2011) and 5:1 (Zhang et al., 2014) have been reported for the esterification process. However, similar yields of upgraded bio-oil (approx. 60%) have been obtained using 2 wt.% sulphuric acid and lower ethanol to oil ratios ranging from 1:1 to 3:1 (Abdul Aziz et al., 2017). Sugar cane, maize and sugar beet are suitable sources for producing bioethanol (Muñoz et al., 2014). For the purposes of this study, bioethanol produced from maize, as given by the Ecoinvent database, has been used. Esterification of the bio-oil in super-critical conditions (250–300^{o}C) has not been considered as it can affect bio-oil composition (Peng et al., 2009). Based on a specific heat capacity of 2.435 kJ/kg of bio-oil, neglected heat losses, an initial bio-oil temperature of 30 °C and the possible operating temperature values, the energy requirement is expected to range from 0.027–0.095 kWh/kg.

2.2.5 Ketonisation

Ketonisation can be performed on the light oxygenates fraction of the pyrolysis oil at around 400 ^{o}C (Snell et al., 2013). The quantity of electricity required in the process is calculated to be 0.25 kWh/kg of light oxygenates. The acetone yield obtained through ketonisation depend on the catalyst, temperature and reaction time, but it is expected to be around 46% using a $Ru/TiO_2/C$ catalyst at 5 wt% (Pham et al., 2012); 349g CO_2 would be formed based on the reaction stoichiometry.

Phase separation of bio-oil into light oxygenate, sugar derived and lignin derived components can be achieved by processing biomass at 300°C to get acetic acid and acetol. This is followed by heating at 400°C to obtain furfurals, and finally processing at 550°C to get phenolics (Pham, Shi and Resasco, 2014). The additional energy requirements at the pyrolysis stage to achieve phase separation have not been included. Separation is expected to obtain 10% light oxygenate, 30% sugar derived and 60% lignin derived components (Pham et al., 2013; Zhang et al., 2007).

2.2.6 Aldol condensation

Aldol condensation takes place at 120°C; 5 wt% Pd/MgO–ZrO2 catalyst is used to process acetone from ketonisation of the light oxygenates and sugar derived oils having undergone esterification (Barrett et al., 2006). The yield from aldol condensation is expected to be 51.4% (Pham, Shi and Resasco, 2014).

2.2.7 Hydrotreating and hydrocracking

Single-stage hydrotreating is usually conducted for 4 hours using noble metal catalysts (Ru/C and Pd/C) and pressures and temperature of up to 200 bar and 400°C (Wildschut, 2009). Hydrotreating of fast pyrolysis oils at 180–250°C and pressures of 130-142 bar using ruthenium have been found to reduce oxygen content from around 40 to 18–27 wt% (Wildschut, 2009; Wang, Male and Wang, 2013). Upgraded bio-oil yields reported for

hydrotreating are more variable and range from 30–65% (Wright et al., 2010; Wildschut, 2009; Holmgren et al., 2008) with the highest yields being obtained when using 5 wt% Ru/C. Hydrotreating pyrolysis oils obtained from corn stover using an Ru/C catalyst can achieve a 25–26 wt% oxygenated product and yields between 54–67% (Capunitan and Capareda, 2014). Hydrogen consumption for corn stover has been reported to range between 69 and 128 litres per litre of feed; higher values of 205 and 252 litres of hydrogen per litre of feed have been reported for mixed wood and poplar (Dang, Yu and Luo, 2014; Elliott et al., 2009).

Two-stage hydrotreating involves performing mild hydrotreating at 150-270^{o}C/80-100 bar, followed by moderate processing at 350–425^{o}C/140–200 bar (Jones et al., 2013). The total residence times for two-stage hydrotreating range from 2 to 4 hours (Jones et al., 2013; Wildschut, 2009). In the first stage, Ru/C is used, whereas a Pt/C or NiMo catalyst is normally used in the second stage. Catalyst quantities are normally around 3–5 wt% (Wildschut et al., 2009; Wildschut, Melián-Cabrera and Heeres, 2010) with lifetimes of 700 to 1752 hours (Snowden-Swan et al., 2016). Therefore, the expected catalyst requirement is 0.1–0.3 g/kg of bio-oil, based on a 4 hour residence time. Reports have claimed that two-stage hydrotreating enables a 13% reduction in hydrogen to be achieved (Gandarias and Arias, 2013), whereas other studies have found the hydrogen consumption to remain proportional to the level of deoxygenation (Boscagli et al., 2015). The amount of deoxygenation can be as low as 2 wt% (Han et al., 2011), but 6–11 wt% is more likely (Wang, Male and Wang, 2013; Wildschut et al., 2009). Hydrogen consumption is expected to range from 58 g/kg (Jones et al., 2013) to 112 g/kg of hydrotreated biofuel (Jones et al., 2009). Other authors have reported 69 g/kg (Dang, Yu and Luo, 2014). The assumption is made that hydrogen is obtained from conventional steam reforming of natural gas; however, make-up hydrogen could be obtained from the off-gases from the pyrolysis and hydroprocessing stages. The overall yield of deoxygenated bio-oil for two-stage

hydrotreating is expected to range from 30–44% (Jones et al., 2009; Zheng, Chang and Fu, 2015).

Hydrocracking is performed at temperatures between 400–450^{o}C and at 100–140 bar (Wright et al., 2010). The catalysts used in the process are 3–5 wt% Ni-HZSM-5 zeolites (Weng et al., 2015). Hydrogen consumption can fluctuate between 1.5 wt% to 4.0 wt% (JSC SIE Neftehim, 2015). Output bio-oil yields of 75% are expected (Sayles and Romero, 2011). The amount of deoxygenation after hydrocracking is expected to range from 0.3–5 wt% (Wildschut et al., 2009; Elliott and Neuenschwander, 1997; Elliott et al., 2009).

The electricity requirement largely depends on the assumptions made regarding processing temperatures, times and heat losses, pressurisation and pumping. Electricity requirements for hydrotreating and hydrocracking have been reported to be 0.23 kWh/kg (Dang, Yu and Luo, 2014) and 0.22 kWh/kg of produced biofuel (Zhang, 2014). Electric energy requirements are very low where the exothermic hydrotreating reactions are considered and values of only 0.034 kWh/kg and 0.054 kWh/kg have been asserted for two-stage hydrotreating and hydrocracking respectively (Iribarren, Peters and Dufour, 2012).

2.2.8 Transportation and distribution of biofuel

The biofuel transportation and distribution was assumed to be via a 9.3t payload truck travelling a total distance of 150 km. Minimum and maximum values of 100 km and 200 km are used to account for the possible range in travelled distance.

A summary of the inventory data is given in Table 2.

3. Results and discussion

The expected carbon dioxide equivalent emissions associated with the production (well-to-tank) and use (tank-to-wheel) of synthetic fuel from pyrolysis are shown for each upgrading scenario in Figure 3; the CO_2 absorbed during biomass growth is shown separately and based

on corn stover absorbing 0.83 kgCO_2/kg (Zan et al., 2001). For comparison, the emissions associated with fossil fuel are provided. Error bars indicate the most optimistic results based on a combination of the most favourable inventory data values.

For synthetic fuel obtained from hydrotreating and hydrocracking pyrolysis oil (scenario 1), the expected production emissions of 2240 gCO_{2e}/kg of upgraded fuel are around 50% of the well-to-wheel CO_{2e} emissions associated with diesel or petrol fuel. The well-to-tank emissions are relatively low for fossil fuel at around 307–659 gCO_{2e}/kg, but the tank-to-wheel emissions are significantly higher at approximately 3387–3571 gCO_2/kg (Eriksson and Ahlgren, 2013). The CO_2 emissions released during the combustion of synthetic fuel depends on carbon content and they can be considered carbon neutral; carbon contents of 77-89% have been reported for various degrees of hydrodeoxygenation (Mante et al., 2016) and tank-to-wheel emissions are expected to range from 2850-3200 gCO_2/kg of fuel (Zhang, 2014; Han et al., 2011).

Scenario 1 is the most commonly considered pyrolysis oil upgrading pathway in the literature. The upgraded fuel from scenario 1 is expected to have a lower heating value of 42 MJ/kg (Peters, Iribarren and Dufour, 2015), which would suggest an impact of 53.6 gCO_{2e}/MJ. This finding is comparable with values reported for similar systems: 39.4–55 gCO_{2e}/MJ has been suggested by other researchers for biofuel from corn stover (Zhang, 2014; Dang, Yu and Luo, 2014). Peters et al. (2015) use a well-to-wheel approach to determine the net emissions from synthetic fuels to be 40 gCO_{2e}/MJ. Other studies provide values of 38.9 gCO_{2e}/MJ when using hybrid poplar (Snowden-Swan and Male, 2012) and 33.3gCO_{2e}/MJ for southern pine (Jones et al., 2013). However, this study reveals the additional CO_{2e} emissions that will arise from further upgrading to improve fuel quality.

The additional upgrading steps in scenarios 2-6, make the CO_{2e} emissions comparable or greater than those associated with using fossil fuel. For example, the emissions caused by producing biofuel in scenario 6 are 43% higher than the total CO_{2e} emissions from diesel fuel. The potential to reduce the CO_{2e} emissions is significant though, as evidenced by the large errors bars. Under more optimistic conditions, the different scenario production emissions range from 1160 to 2930 gCO_{2e}/ kg, which represent a potential decrease of 47% to 52%. However, scenario 6 appears favourable when considering a well-to-wheels analysis including the CO_2 absorbed, as 12.2 kg of corn stover is required to produce 1 kg of biofuel in scenario 6, whereas, in scenario 1, only 3.8 kg of corn stover is required.

Further details on the downstream use of the various by-products from the different processing stages are required to give a more accurate representation of the net emissions. When the non-condensable gases are flared or used for heat recovery, up to 17% of the feedstock carbon could be released back into the atmosphere (Mullen et al., 2010), and these emissions are not included in the production emissions. Biochar can act as a long-term carbon sink enabling as much as 20% of the carbon to be recovered during fast pyrolysis (ibid). If the char were combusted to meet the thermal energy requirement in the pyrolysis reactor, credits can be applied to account for the offset fossil fuel requirement; however, the use of electricity is more practical.

Figure 4 shows the CO_{2e} emission contributions from the use of electricity, hydrogen, transport, fertilisers, catalysts, ethanol and natural gas. Minimum, expected and maximum values are shown for each scenario. Electricity is the largest contributor with a 50–63% expected share of the total emissions. However, for optimistic conditions, the emissions associated with the use of electricity are reduced by around 70%. At 17-33%, the second largest CO_{2e} contribution comes from the use of hydrogen. These CO_{2e} emissions could be reduced by around 25–29% based on the range of hydrogen consumption values reported in

the literature. Fertilisers, transport and catalysts contribute respectively 14–17%, 2.2% and 1.2–3% of the total CO_{2e} emissions. Net CO_{2e} emissions from using ethanol obtained from maize in the US are slightly carbon negative (-20 to -70 gCO_{2e}/kg) and the source of ethanol can influence the results significantly.

The total CO_{2e} emissions from each stage of the system are shown in Figure 5. The expected CO_{2e} emissions prior to bio-oil upgrading are significant with cultivation, pre-treating and pyrolysis accounting for around 54-64% of the emissions. In an optimistic scenario, e.g. where energy recovery or alternative energy sources to electricity can be used, the share of emissions from pyrolysis are reduced by approximately 74%.

The high proportion of CO_{2e} emissions associated with hydrogen and electricity highlight the importance of using more sustainable alternatives, which could also reduce operating costs. Moreover, as the pyrolysis and hydroprocessing stages made the most significant contribution to the total CO_{2e} emissions, this identifies that these stages would benefit the most from R&D to achieve gains in environmental and technical performance. The average EU27 electricity grid mix has been used in this study; however, alternative sources such as natural gas, pyrolysis gases and other renewables can be considered.

The pessimistic inventory data provided in this study reveals that the emissions for scenarios 1–6 are around 1.5 to 3 times higher than fossil fuel, which is a major concern if facilities and supply chains conduct inefficient practices. This result also highlights the large uncertainty that remains in this field with determining the environmental benefits of using synthetic fuels obtained from the thermochemical conversion of waste feedstocks, and the need for better quality primary data on bio-oil upgrading system performance.

Other environmental impacts occurring from the production of fuels (well-to-tank) according to the CML 2001 impact assessment method are summarised in Table 3. Minimum and

expected impacts for scenarios 1-6 are shown in comparison to low sulphur diesel fuel from the Ecoinvent database. Whereas scenario 1 provides environmental advantages over diesel, scenarios 2-6 increase several negative environmental impacts. For scenarios 2-6, the expected eutrophication and acidification potentials range respectively from 0.0026–0.005 kg PO_4^{3-} eq. and 0.0098–0.027 kg SO_2 eq., which are higher than the impacts associated with diesel fuel (0.00167 kg PO_4^{3-} eq and 0.0058 kg SO_2 eq.). In all scenarios, the expected human and eco toxicity potentials are also higher than diesel fuel. These results are to be expected due to the high quantities of fertiliser and other material and energy resources used in scenarios 2-6.

Different farming practices can heavily influence the fertiliser requirements. The sensitivity of the GWP and eutrophication result based on ammonium nitrate usage in scenario 1 is further examined in Figure 6a. It shows that the eutrophication potential would be reduced to 0.00061 kg PO_4^{3-} eq if ammonium nitrate fertiliser were avoided. The element abiotic depletion potential (ADP) is also high in all scenarios as a result of fertiliser usage. Interestingly, the fossil ADP value is also higher than diesel fuel in scenarios 2-6, which is caused by the increased hydrogen consumption in the more advanced upgrading processes. However, the minimum values reveal that savings could be achieved with the exception of scenario 6. The sensitivity of the GWP and fossil ADP values based on the hydrogen consumption in scenario 1 is shown in Figure 6b. An increase in hydrogen consumption from 50 to 168 g/kg of upgraded fuel doubles the fossil ADP and increases the GWP from around 1.9 to 2.8 kg $CO_{2e.}$ Whilst conventional externally sourced hydrogen from natural gas has been considered in this study, other authors have suggested that internal steam reforming of by-products to produce hydrogen is a more promising option (Dang, Yu and Luo, 2014).

Future LCA studies on synthetic fuels must consider the wide range of environmental impacts that occur during the production of synthetic fuels, as many negative environmental

impacts increase in comparison to the diesel and petrol production processes. In further work, the materials used in system construction could also be taken into account. Different allocation methods for stover and pyrolysis by-products need to be investigated to see if environmental benefits can be gained. For example, economic and energy-based allocation methods have been compared for corn and stover production (Murphy and Kendall, 2013). A displacement approach could also be considered as corn stover would likely be used elsewhere (e.g. as cattle feed). As more and more companies seek to commercialise the production of synthetic fuel via pyrolysis, great care must be taken to ensure that environmental gains over conventional fossil fuels are being achieved and a trade-off between environmental impact, cost and product quality has to be made.

4. Conclusion

This study identifies that favourable CO_{2e} emission reductions can be achieved by using synthetic fuel from pyrolysis in comparison to conventional diesel fuel. However, if inefficient practices are followed, a low quality synthetic fuel that nearly triples CO_{2e} emissions in comparison to fossil fuel will be produced. High quality fuels obtained via esterification, two-stage hydrotreating and hydrocracking, or esterification, ketonisation, adol condensation, two-stage hydrotreating and hydrocracking, are expected to increase a range of other environmental impact indicators. Esterification and single-stage hydrotreating (scenario 2) or two-stage hydrotreating (scenario 4) can provide a reasonable trade-off between product quality and achievable environmental gains.

Figures and Tables

Figure 1: Life cycle system boundaries for the production and use of synthetic fuels from fast pyrolysis and fossil fuel.

Figure 2: Six alternative bio-oil upgrading scenarios to produce liquid fuels from pyrolysis.

Figure 3: The CO_{2e} emissions associated with the production and use of synthetic fuel for six different upgrading scenarios. Error bars are used to show the minimum CO_{2e} emissions possible and, under these conditions, less feedstock is required to produce a kilogram of biofuel.

Figure 4: Minimum, expected and maximum CO_{2e} emissions associated with the use of electricity, hydrogen, transport, fertilisers, catalysts, ethanol and natural gas during the production of synthetic fuel from pyrolysis oil.

Figure 5: Minimum, expected and maximum CO_{2e} emissions associated with each processing stage during the production of synthetic fuel from pyrolysis oil.

Figure 6a-b: Sensitivity of the environmental impacts arising from scenario 1 based on ammonium nitrate (a) and hydrogen (b) usage.

Table 1: Summary of the six different bio-oil upgrading scenarios.

Table 2: LCA inventory data for the production of synthetic fuels via fast pyrolysis and upgrading.

Table 3: Environmental impacts conforming to the CML 2001 assessment method for the production of synthetic and diesel fuel.

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Figure 1

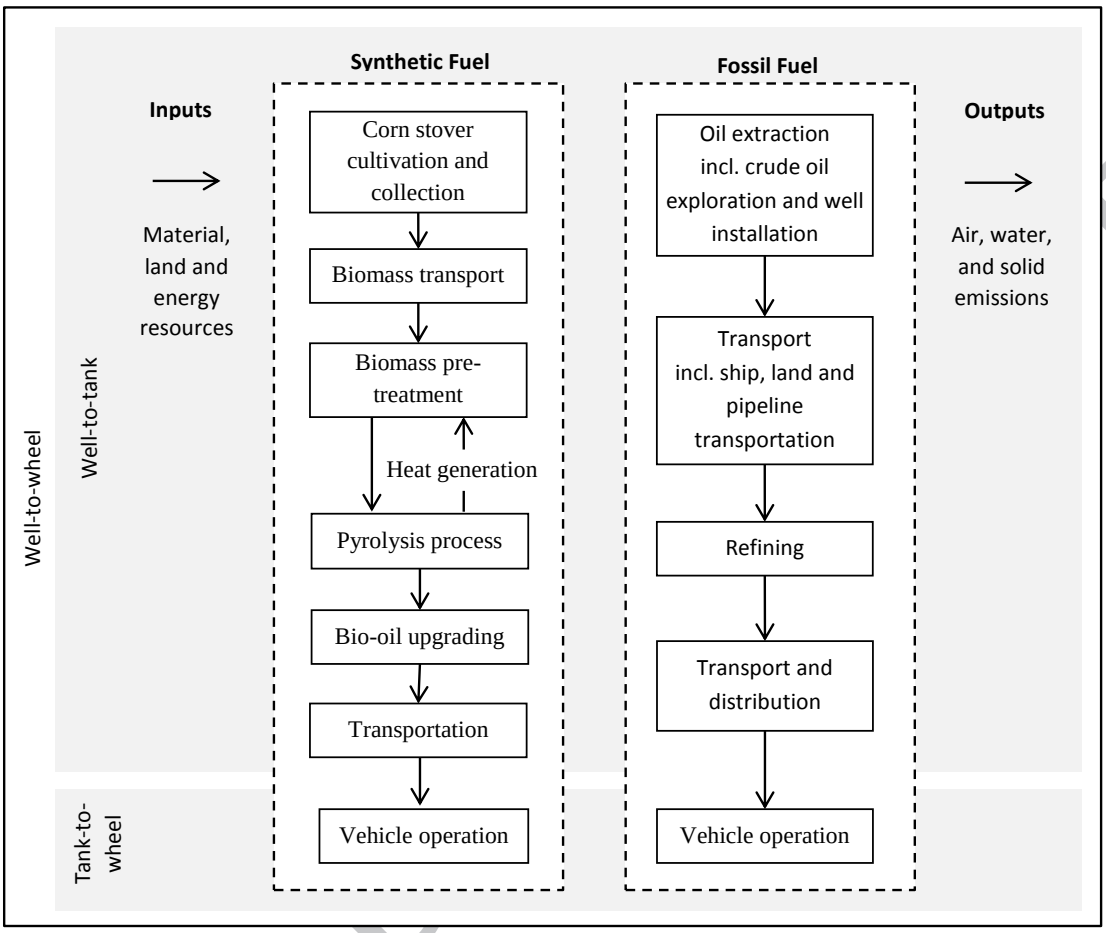


Figure 2

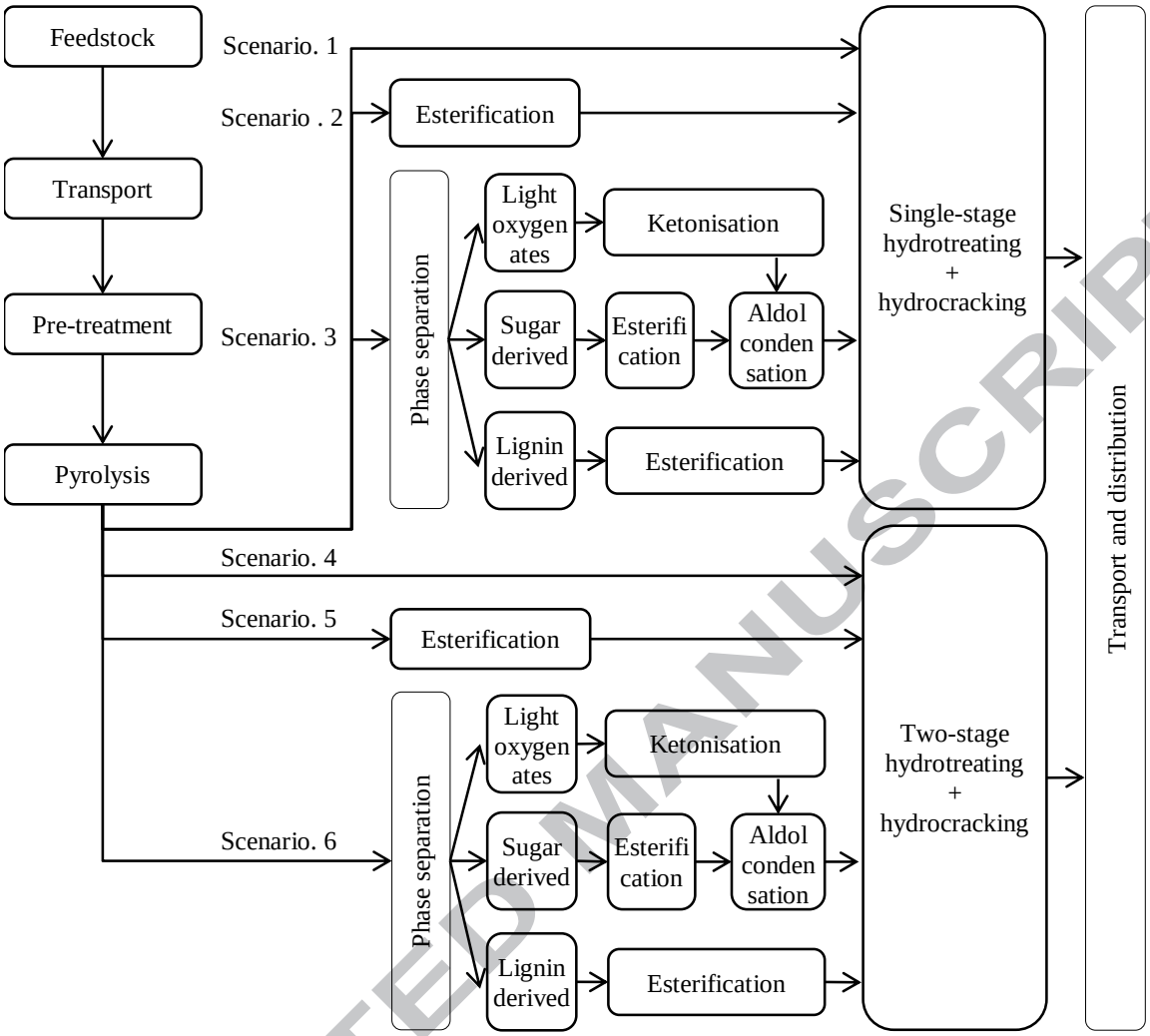


Figure 3

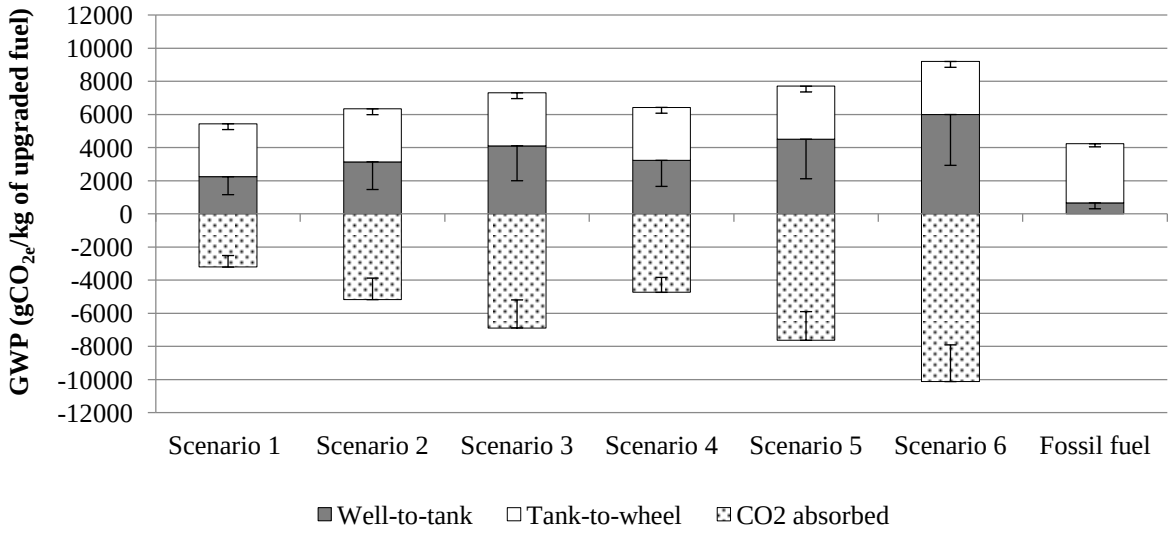


Figure 4

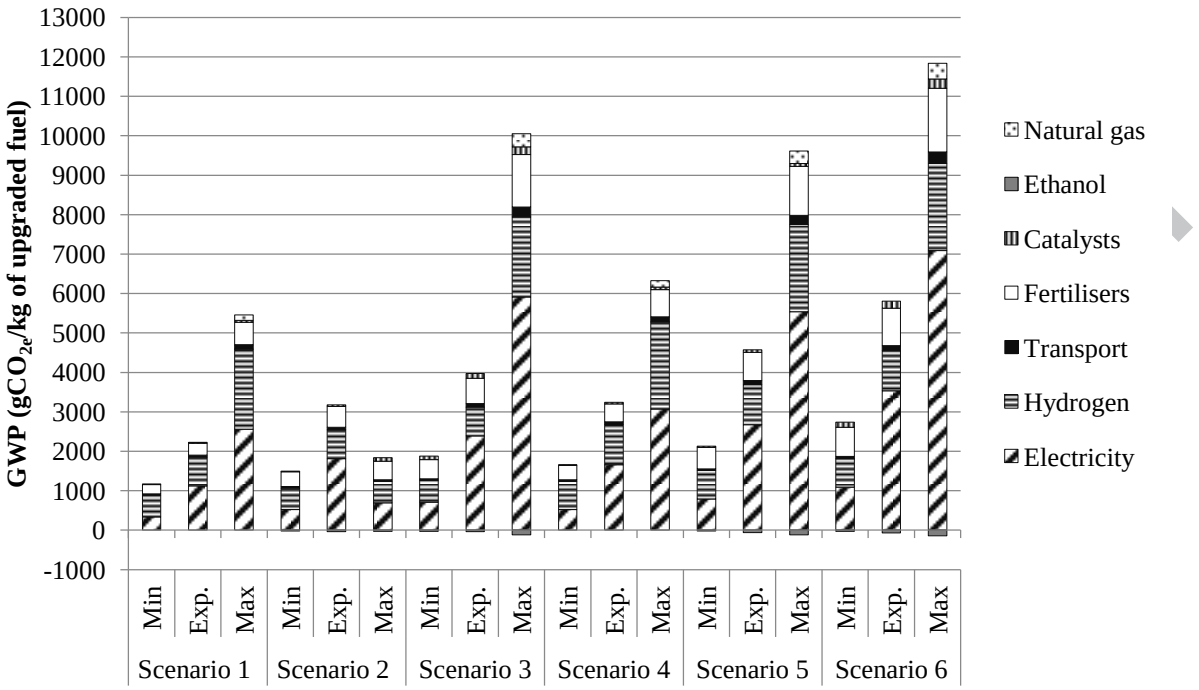


Figure 5

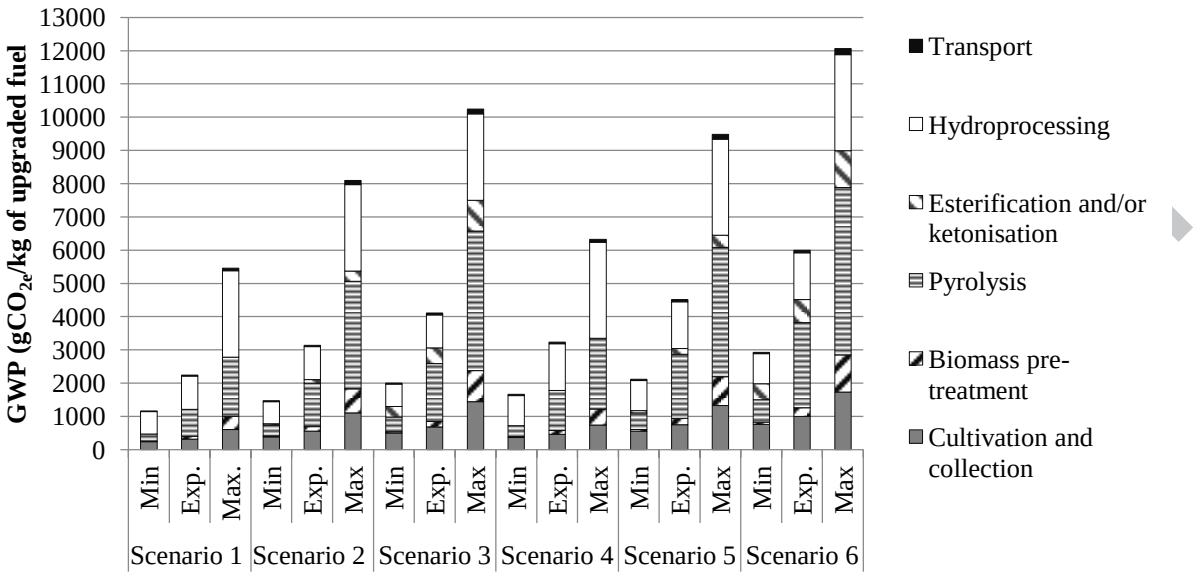
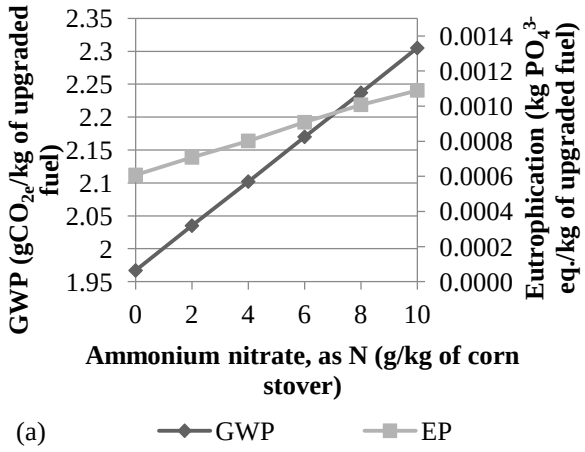
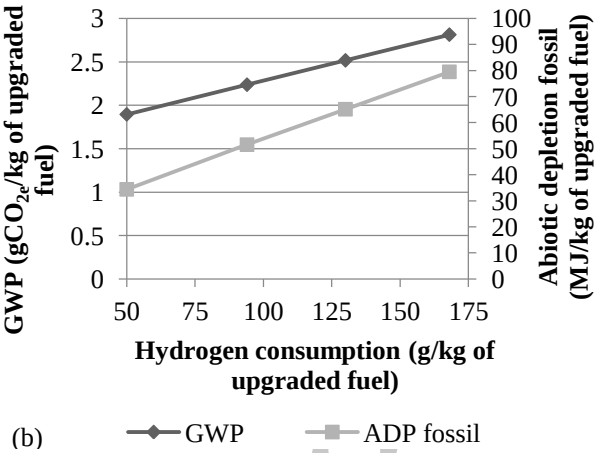


Figure 6





Upgrading scenario	Summary
1. Hydrotreating and hydrocracking	The minimum amount of processing required to obtain a transportation fuel; however, oxygen content is high.
2. Esterification, hydrotreating and hydrocracking	Using esterification prior to hydrotreating and hydrocracking can improve stability and reduce catalytic deactivation and acidification.
3. Esterification, ketonisation, hydrotreating and hydrocracking	Esterification and ketonisation improve stability and neutralise carboxylic acids.
4. Two-stage hydrotreating and hydrocracking	Two-stage hydrotreating can further reduce bio-oil oxygen content.
5. Esterification, two-stage hydrotreating and hydrocracking	Reducing acidity and improving stability of a bio-oil prior to hydrotreating will improve reliability and potentially reduce hydrogen consumption.
6. Esterification, ketonisation, two-stage hydrotreating and hydrocracking	The most comprehensive combination of upgrading processes to produce a stable biofuel with a low oxygen and acidic component content.

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Feedstock cultivation and collection	**Min**	**Expected**	**Max**	**Unit**	**Ref.**
Fossil energy	0.22	0.53	0.83	MJ/kg of corn stover	[8, 32]
Ammonium nitrate phosphate, as P_2O_5	-	2	-	g/kg of corn stover	[32, 33]
Potassium chloride, as K_2O	-	14.5	-	g/kg of corn stover	[32, 33]
Ammonium nitrate, as N	-	8	-	g/kg of corn stover	[32, 33]
Biomass transportation	**Min**	**Expected**	**Max**	**Unit**	
Diesel	0.05	0.075	0.1	MJ/kg of delivered corn stover	[13]
Pre-treatment	**Min**	**Expected**	**Max**	**Unit**	
Electricity for grinding	0.011	0.034	0.057	kWh/kg of pre-treated corn stover	[27, 53]
Steam from natural gas boiler	0	0	0.085	kg/kg of pre-treated corn stover	[53]
Prepared feedstock yield	-	82	-	%	[8, 49]
Pyrolysis process	**Min**	**Expected**	**Max**	**Unit**	
Electricity	0.14	0.417	0.487	kWh/kg of produced bio-oil	[8, 53]
Pyrolysis oil yield	62	75	80	%	[5, 8, 17]
Esterification	**Min**	**Expected**	**Max**	**Unit**	
Electricity	0.027	0.061	0.095	kWh/kg of raw bio-oil	-
Sulphuric acid	-	2	-	wt%	[1]
Ethanol	1	2	3	kg/kg of raw bio-oil	[1]
Biofuel yield	55	62	65	%	[1, 34]
Ketonisation	**Min**	**Expected**	**Max**	**Unit**	
Electricity	-	0.25	-	kWh/kg of light oxygenates	-
$Ru/TiO_2/C$ Catalyst	-	5	-	wt%	[38]
Acetone yield	-	46	-	%	[38]
Hydroprocessing	**Min**	**Expected**	**Max**	**Units**	
Single-stage HT hydrogen consumption	69	74	128	g/kg of HT biofuel	[8, 11]
Ru/C Catalyst (first-stage)	0.1	0.2	0.3	g/kg of HT biofuel	[47]
Single-stage HT yield of 18-27 wt% deoxygenated biofuel	36	56	67	%	[6, 18, 47, 49]
Two-stage HT hydrogen consumption	58	69	112	g/kg of HT biofuel	[22, 23]
Pt/C/ Pd/C Catalyst (second-stage)	0.1	0.2	0.3	g/kg of HT biofuel	[46, 48]
Two-stage HT yield of 2-11 wt% deoxygenated biofuel	30	38	44	%	[22, 54]
HC hydrogen consumption	15	20	40	g/kg of HC biofuel	[24]
Zeolite powder for HC	3	5	5	wt%	[45]
HC biofuel yield	-	0.75	-	kg/kg of HC biofuel	[40]
Total electricity for hydroprocessing	0.088	0.16	0.23	kWh/kg of biofuel	[8, 20, 53]
Fuel transportation	**Min**	**Expected**	**Max**	**Unit**	
Diesel	0.1	0.15	0.2	MJ/kg of delivered biofuel	[13]

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Impact Categories	Scenario 1		Scenario 2		Scenario 3		Scenario 4		Scenario 5		Scenario 6		Diesel
	Min	Exp.	Min	Exp.	Min	Exp.	Min	Exp.	Min	Exp.	Min	Exp.	
Acidification Potential (kg SO_2 eq.)	2.80E-03	4.95E-03	4.88E-03	9.78E-03	1.20E-02	1.80E-02	4.04E-03	7.18E-03	7.22E-03	1.40E-02	1.70E-02	2.70E-02	5.82E-03
Eutrophication Potential (kg PO_4^{3-} eq.)	6.18E-04	1.01E-03	1.26E-03	2.61E-03	1.84E-03	3.34E-03	9.16E-04	1.47E-03	1.90E-03	3.57E-03	2.78E-03	4.91E-03	1.67E-03
Ozone layer depletion potential (kg R11 eq.) [a]	1.91E-08	2.70E-08	4.17E-08	7.56E-08	6.01E-08	9.58E-08	2.91E-08	3.99E-08	6.35E-08	1.03E-07	9.24E-08	1.41E-07	6.90E-07
Abiotic depletion element (kg Sb eq.)	1.68E-06	2.65E-06	2.87E-06	5.00E-06	4.78E-06	7.51E-06	2.52E-06	3.90E-06	4.33E-06	7.15E-06	7.25E-06	1.10E-05	4.74E-07
Abiotic depletion fossil (MJ)	3.26E+01	5.16E+01	3.73E+01	6.52E+01	4.14E+01	7.41E+01	4.44E+01	7.31E+01	5.15E+01	9.25E+01	5.77E+01	1.07E+02	5.36E+01
Freshwater aquatic ecotoxicity potential (kg DCB eq.) [b]	6.20E-02	9.50E-02	1.24E-01	2.39E-01	2.15E-01	3.45E-01	9.30E-02	1.40E-01	1.89E-01	3.28E-01	3.27E-01	5.09E-01	8.60E-02
Human toxicity Potential (kg DCB eq.)	1.81E-01	2.75E-01	3.15E-01	5.51E-01	4.37E-01	7.10E-01	2.70E-01	4.03E-01	4.75E-01	7.79E-01	6.61E-01	1.04E-00	2.71E-01
Marine aquatic ecotoxicity potential (kg DCB eq.)	2.27E+02	3.96E+02	4.11E+02	8.46E+02	6.09E+02	1.01E+03	3.43E+02	5.82E+02	6.23E+02	1.15E+03	9.24E+02	1.60E+03	2.79E+02
Photochemical oxidant creation potential (kg C_2H_4 eq.)	2.01E-04	3.45E-04	3.01E-04	5.87E-04	7.51E-04	1.16E-03	2.97E-04	5.06E-04	4.46E-04	8.34E-04	1.012E-03	1.71E-03	5.72E-04
Terrestric ecotoxicity potential (kg DCB eq.)	2.55E-03	3.92E-03	5.16E-03	9.98E-03	7.02E-03	1.20E-02	3.87E-03	5.75E-03	7.84E-03	1.40E-02	1.10E-02	1.80E-02	3.43E-03

[a] Trichlorofluoromethane equivalent (R11 eq.)

[b] Dichlorobenzene equivalent (DCB eq.)

623 Highlights

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625 • The environmental impacts of six different bio-oil upgrading scenarios are analysed
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627 • Expected, optimistic, and pessimistic values are evaluated
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629 • CO_2 equivalent emissions are expected to range from 2240–6000 gCO_{2e}/kg of biofuel
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631 • A worst-case scenario leads to CO_{2e} emissions tripling in comparison to fossil fuel
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